

# Synthesis of Benzyl Esters via Functionalization of Multiple C–H Bonds by Palladium Catalysis

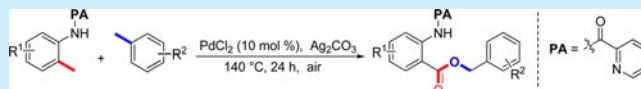
Danyang Li,<sup>†</sup> Ming Yu,<sup>†</sup> Jitan Zhang,<sup>†</sup> Zhanxiang Liu,<sup>\*,†</sup> and Yuhong Zhang<sup>\*,†,‡</sup>

<sup>†</sup>ZJU-NHU United R&D Center, Department of Chemistry, Zhejiang University, Hangzhou 310027, China

<sup>‡</sup>State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China

**S** Supporting Information

**ABSTRACT:** A highly efficient, selective synthesis of benzyl esters by palladium catalysis is developed through the bidentate directing group assisted functionalization of multiple C(sp<sup>3</sup>)–H bonds.

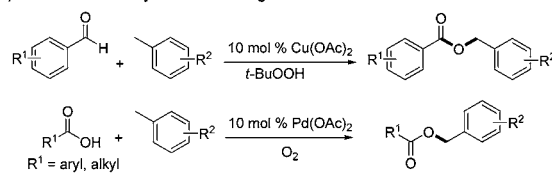


The formation of esters is one of the most fundamental transformations in organic synthesis due to the potential utility of esters in fine chemicals, agrochemicals, polymers, pharmaceuticals, and natural organic molecules.<sup>1</sup> Accordingly, the efficient synthesis of esters has attracted considerable interest. In general, the nucleophilic reactions of carboxylic acids and their derivatives with alcohols/halohydrocarbons are reliable methods for the preparation of esters.<sup>2</sup> However, these protocols require the prefunctionalization of substrates and often suffer from harsh reaction conditions. To overcome these disadvantages, much effort has focused on transition-metal-catalyzed oxidative C–H bond cleavage for the assembly of esters.<sup>3</sup> In particular, the catalytic esterification of benzylic sp<sup>3</sup> C–H bonds has recently become a hot topic due to the importance of benzyl esters,<sup>4</sup> and pioneering work on the synthesis of benzyl esters from toluene has been reported.<sup>5</sup> For instance, the Patel group developed the copper-catalyzed cross dehydrogenative coupling (CDC) reaction of aryl aldehydes with toluene for the synthesis of benzyl esters using *tert*-butyl hydroperoxide (TBHP) as the oxidant, in which the benzylic sp<sup>3</sup> C–H bond of toluene was oxidized to benzyl alcohol *in situ* and dual C–H oxidative cross coupling was achieved.<sup>6a</sup> Later, the direct benzylation of carboxylic acids by toluene under oxygen was reported by Zhang and co-workers using palladium catalysis.<sup>6b</sup> In these transformation, the direct esterification of toluene with aldehydes or carboxylic acids is successfully achieved (Scheme 1, a). In principle, the most direct route for access to benzyl esters is the selective benzylation of toluene with another alkylbenzenes. However, successful esterification between two different alkylbenzenes is far more elusive: (1) toluene can react not only with itself but also with another different alkylbenzene, and (2) the benzylic C–H bond can be oxidized not only to the corresponding hydroxyl but also to the corresponding aldehyde.

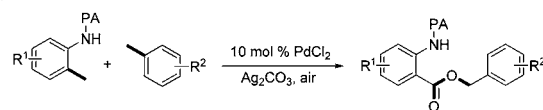
The chelation-assisted transition-metal-catalyzed functionalization of C–H bonds has emerged as a powerful tool for the construction of C–C and C–X bonds.<sup>7</sup> To date, several methods for the direct, catalytic functionalization of benzylic sp<sup>3</sup> C–H bonds, such as alkenylation and amidation, have been reported.<sup>8</sup> Recently, we studied the palladium-catalyzed arylation/oxida-

## Scheme 1. Examples of Catalytic Synthesis of Benzyl Esters

### a) Previous work by Patel and Zhang



### b) This work

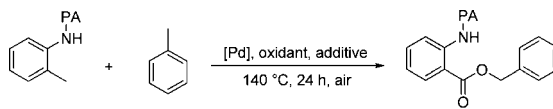


tion<sup>9a</sup> and oxidative acetoxylation of benzylic C–H bonds with the assistance of a bidentate auxiliary.<sup>9b</sup> We envisioned that the introduction of a directing group in the alkylbenzenes might allow the selective oxidation of a benzylic C–H bond to achieve esterification between two different alkylbenzenes. As the first attempt, a mixture of picolinoyl-protected toluidene **1a** and toluene **2a** was treated with 10 mol % of Pd(OAc)<sub>2</sub> catalyst and 2 equiv of Ag<sub>2</sub>CO<sub>3</sub> as an oxidant at 140 °C in air. The esterification product **3a** was indeed obtained in 23% yield after 24 h (Table 1, entry 1). This catalytic reaction was found to be powerful enough to generate the benzyl ester through multiple benzylic C–H bond cleavages. Furthermore, this transformation exhibits high selectivity: the byproducts of the benzylation of toluene with **1a** and the benzylation of toluene with itself were not observed. Thus, the selective palladium-catalyzed benzylation of alkylbenzenes with toluene is achieved with the assistance of a bidentate auxiliary (Scheme 1, b).

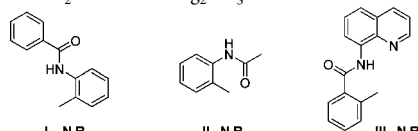
To optimize the reaction conditions, a variety of palladium catalysts were examined. It was found that the use of Pd(TFA)<sub>2</sub> and Pd<sub>2</sub>(dba)<sub>3</sub> also gave the esterification product **3a** as the main product, but in low yields (Table 1, entries 2 and 3). Among the palladium sources examined, PdCl<sub>2</sub> was found to be the most efficient catalyst (Table 1, entry 4). Silver carbonate was proved

Received: September 15, 2015

Published: October 13, 2015

Table 1. Optimization of Reaction Conditions<sup>a</sup>


entry	catalyst	oxidant	additive	yield <sup>b</sup> (%)
1	Pd(OAc) <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>		23
2	Pd(TFA) <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>		21
3	Pd <sub>2</sub> (dba) <sub>3</sub>	Ag <sub>2</sub> CO <sub>3</sub>		20
4	PdCl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>		28
5	PdCl <sub>2</sub>	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>		NR
6	PdCl <sub>2</sub>	BQ		NR
7	PdCl <sub>2</sub>	TBHP		NR
8	PdCl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	HOAc	32
9	PdCl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	PivOH	43
10	PdCl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	TFA	trace
11	PdCl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	OTA	55
12	PdCl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	OTA	64 <sup>c</sup>
13	PdCl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	OTA	0 <sup>d</sup>
14	PdCl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	OTA	0 <sup>e</sup>
15	PdCl <sub>2</sub>	Ag <sub>2</sub> CO <sub>3</sub>	OTA	48 <sup>f</sup>

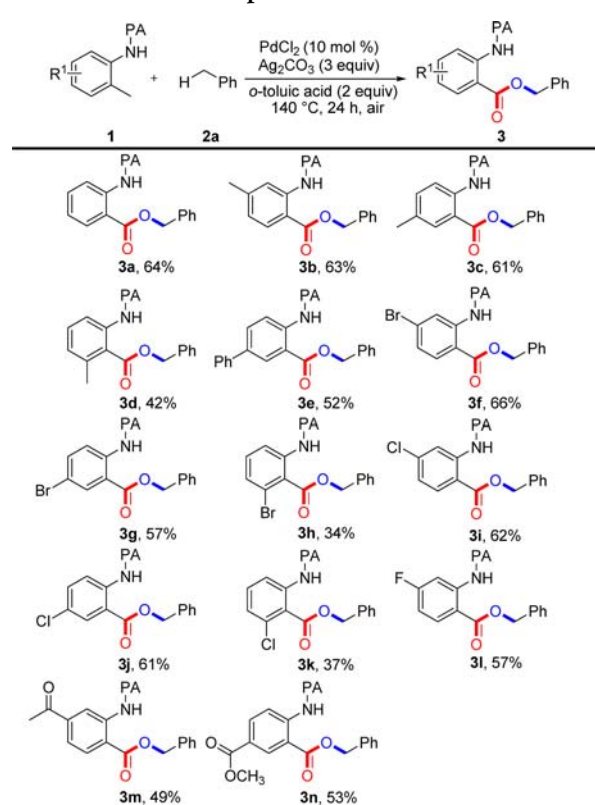


<sup>a</sup>Reaction conditions: **1a** (0.2 mmol), **2a** (3.0 mL), PdCl<sub>2</sub> (0.02 mmol), oxidant (0.4 mmol), and additive (0.4 mmol) under air at 140 °C for 24 h. <sup>b</sup>Isolated yield by flash column chromatography. <sup>c</sup>0.6 mmol of Ag<sub>2</sub>CO<sub>3</sub> was used. <sup>d</sup>Without PdCl<sub>2</sub>. <sup>e</sup>Under N<sub>2</sub> atmosphere. <sup>f</sup>Under O<sub>2</sub> atmosphere. PA = 2-pyridylacetyl, OTA = *o*-toluic acid.

to be the best oxidant (Table 1, entry 4). Other oxidants, such as K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, benzoquinone (BQ), and *tert*-butyl hydroperoxide (TBHP), were entirely ineffective (Table 1, entries 5–7). The addition of acid was particularly effective, and *o*-toluic acid was superior, giving the esterification product **3a** in 55% yield (Table 1, entries 8–11). After further investigation, we were pleased to find that the isolated yield of **3a** was improved to 64% by using 3 equiv of Ag<sub>2</sub>CO<sub>3</sub> (Table 1, entry 12). No desired esterification product was observed in the absence of palladium catalyst (Table 1, entry 13), and the reaction failed in a nitrogen atmosphere (Table 1, entry 14). In addition, the yield of **3a** was decreased when the reaction was performed under O<sub>2</sub> atmosphere. A possible reason is that the toluene may be oxidized to benzaldehyde rapidly under the pure O<sub>2</sub> atmosphere, which hinders the generation of ester (Table 1, entry 15).

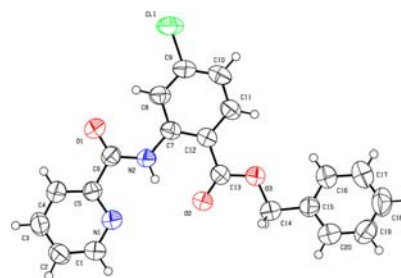
The directing group was found to be crucial for this esterification transformation. No reaction occurred when benzamide **I** or acetamide **II** was used as the substrate, illustrating that bidentate coordination was essential for the reaction. 8-Aminoquinolinamide **III**, which possesses the popular directing group of bidentate 8-aminoquinoline auxiliary, also failed to give the desired ester, showing the predominant power of picolinamide as the directing group in this esterification reaction.

With the optimal conditions in hand, we next investigated the scope of picolinamide arene substrates as shown in Scheme 2. In general, arenes bearing both electron-donating and electron-withdrawing groups reacted well under the optimized conditions. For instance, the electron-rich arenes generated the corresponding benzyl esters in high yields (**3a–d**). A picolinamide arene with a phenyl group at the *para* position participated smoothly in

Scheme 2. Substrate Scope of Picolinamides<sup>a,b</sup>

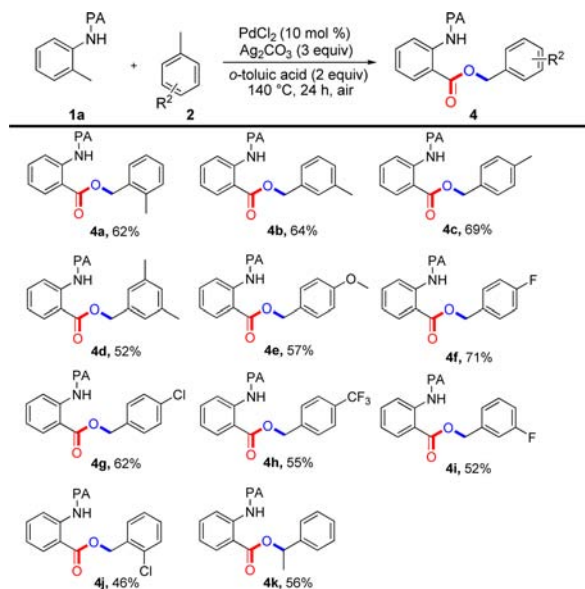
<sup>a</sup>Isolated yields are given. <sup>b</sup>Reaction conditions: **1** (0.2 mmol), **2a** (3 mL), PdCl<sub>2</sub> (0.02 mmol), Ag<sub>2</sub>CO<sub>3</sub> (0.6 mmol), 140 °C, air, 24 h. PA = 2-pyridylacetyl.

the reaction to give the desired product in 52% yield (**3e**). Notably, C–Cl and C–Br bonds remained intact during the reaction (**3f–k**), providing an additional opportunity for further elaboration of the products by cross-coupling reactions. Picolinamide arenes with strong electron-withdrawing groups, such as fluoro, acetyl, and ester groups, were good substrates for this esterification reaction, affording the corresponding benzyl esters in good yields (**3l–n**). The sterically hindered arenes were slightly disfavored, delivering the corresponding products in relatively lower yields (**3h** and **3k**). The selectivity of this transformation was that the three C–H bonds of the methyl group in toluene were thoroughly oxidized to generate the benzoyl moiety of the esters, and only one C–H bond in toluene was cleaved to provide the benzyloxy portion in the formed esters. X-ray crystallographic analysis of **3i** further confirmed the structure of this esterification reaction product (Figure 1).

Figure 1. ORTEP drawing of **3i**.

We subsequently applied this new esterification method to diverse alkylbenzene substrates, as shown in Scheme 3.

### Scheme 3. Substrate Scope of Alkylbenzenes<sup>a,b</sup>

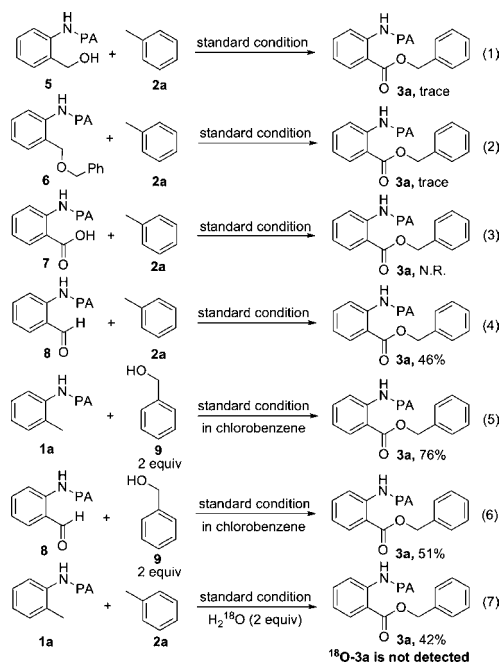


<sup>a</sup>Isolated yields are given. <sup>b</sup>Reaction conditions: **1a** (0.2 mmol), **2** (3 mL), PdCl<sub>2</sub> (0.02 mmol), Ag<sub>2</sub>CO<sub>3</sub> (0.6 mmol), 140 °C, air, 24 h. PA = 2-pyridylacetyl.

Gratifyingly, both electron-rich and electron-deficient alkylbenzenes could be smoothly converted to the desired esters in good yields (**4a–k**, 46–71%). The substrates with more than one methyl group, such as xylene (*o*-, *m*-, *p*-) and mesitylene, were examined, and an appealing outcome was obtained in the formation of only monoester product (**4a–d**). The transformation was compatible with common functional groups, including methoxy, fluoro, chloro, and trifluoromethyl groups (**4e–j**). It is worth mentioning that the relatively bulky ethylbenzene could be included in the reaction and exhibited good reactivity (**4k**).

Control experiments were performed to obtain insights into the reaction mechanism (Scheme 4). When picolinamide benzylic alcohol **5** or picolinamide benzylic ether **6** was used as the substrate under the standard conditions, only a trace of the desired product **3a** was observed (eq 1–2). This result demonstrated that neither picolinamide benzylic alcohol nor its ether is involved in the formation of the benzyl ester. In addition, no desired product was observed when 2-(picolinamido)benzoic acid **7** was used as the substrate (eq 3), showing that picolinamide carboxylic acid was not the key intermediate for the formation of the benzyl esters. In contrast, *N*-(2-formylphenyl)picolinamide **8** could participate in the reaction to deliver the desired benzyl ester in 46% yield (eq 4), suggesting that picolinamide benzaldehyde might be an intermediate in the esterification. The esterification reaction of **1a** with benzylic alcohol **9** proceeded smoothly to give the product **3a** in 76% yield (eq 5), confirming that toluene served as the source of the PhCH<sub>2</sub>O– group. Additionally, the reaction of compound **8** and **9** was performed, and the product **3a** was obtained in 51% yield, implicating that compound **8** and **9** might be involved in the reaction (eq 6). Because the reaction failed in a nitrogen atmosphere (Table 1, entry 14) and the <sup>18</sup>O-labeled product was not observed in the existence of H<sub>2</sub><sup>18</sup>O under the reaction

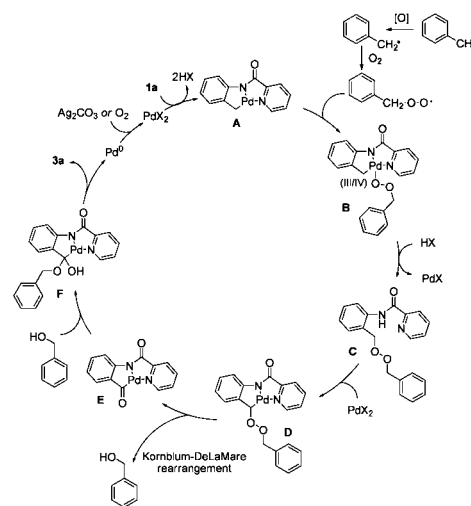
### Scheme 4. Control Experiments



conditions (eq 7), the oxygen in the ester is proved to originate from O<sub>2</sub> in the air. The addition of a radical scavenger 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) to the reaction halted the esterification reaction, indicating that a radical process might be involved in the reaction. In addition, the benzyl radical was trapped by TEMPO (see the Supporting Information).

Based on the above observations and previous investigation, we propose a plausible reaction mechanism for this efficient esterification transformation as shown in Scheme 5. The initial

### Scheme 5. Mechanistic Hypothesis



picolinamide-assisted palladation leads to the formation of palladacycle **A**,<sup>10</sup> which is oxidized by the benzyl peroxide radical to generate the Pd(IV)<sup>11</sup> or dimeric Pd(III)<sup>12</sup> intermediate **B**. The reductive elimination of intermediate **B** results in intermediate **C**, which undergoes the second palladation to give intermediate **D**. The subsequent Kornblum–DeLaMare rearrangement affords intermediate **E**,<sup>13</sup> and the reaction of **E** with benzyl alcohol produces intermediate **F**.<sup>14</sup> MALDI-TOF

mass analysis of the reaction mixture proved the formation of intermediates E and F during the esterification process (see the Supporting Information). Finally, the  $\beta$ -hydrogen elimination and reductive elimination of intermediate F delivers the esterification product (3a) and liberates the Pd(0). The catalytic Pd(II) is then regenerated by oxidation to initiate the next cycle.

In conclusion, we have developed an efficient new protocol for the synthesis of benzyl esters via the palladium-catalyzed selective activation of multiple benzylic C(sp<sup>3</sup>)-H bonds. The bidentate system is proved to be crucial to the successful selective formation of benzyl esters. The oxygen in the ester is proved to originate from O<sub>2</sub> in the air, and the method displays exceptional compatibility with a wide range of functional groups to give benzyl esters selectively in good yields. Further investigations of the detailed mechanism are underway in our laboratory.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02518.

Experimental details, spectral and analytical data, and <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for new compounds (PDF) X-ray data for 3i (CIF)

## ■ AUTHOR INFORMATION

### Corresponding Authors

\*E-mail: liuzhanx@zju.edu.cn.

\*E-mail: yhzhang@zju.edu.cn.

### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

Funding from NSFC (No. 21272205, 21472165) and the Program for Zhejiang Leading Team of S&T Innovation (2011RS0007) is acknowledged.

## ■ REFERENCES

- (1) (a) Otera, J. *Esterification: Methods, Reactions, and Applications*; Wiley-VCH: Weinheim, 2003. (b) Riemenschneider, W.; Bolt, H. M. Esters, Organic. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, 2005. (c) Carmo, A. C.; de Souza, L. K. C.; da Costa, C. E. F.; Longo, E.; Zamian, J. R.; da Rocha Filho, G. N. *Fuel* **2009**, *88*, 461. (d) Kheang, L. S.; May, C. Y. *J. Oil Palm Res.* **2012**, *24*, 1388.
- (2) (a) Larock, R. C. *Comprehensive Organic Transformations: A Guide to Functional Group Preparations*, 2nd ed.; Wiley-VCH: New York, 1999. (b) Haslam, E. *Tetrahedron* **1980**, *36*, 2409. (c) Swamy, K. C. K.; Kumar, N. N. B.; Balaraman, E.; Kumar, K. V. P. *Chem. Rev.* **2009**, *109*, 2551. (d) Luo, F.; Pan, C.; Cheng, J. *Synlett* **2012**, *23*, 357.
- (3) For selected examples, see: (a) Eames, J.; Watkinson, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3567. (b) Desai, L. V.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 9542. (c) Chen, M. S.; Prabakaran, N.; Labenz, N. A.; White, M. C. *J. Am. Chem. Soc.* **2005**, *127*, 6970. (d) Dick, A. R.; Kampf, W. J.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 12790. (e) Chen, X.; Hao, X.-S.; Goodhue, C. E.; Yu, J.-Q. *J. Am. Chem. Soc.* **2006**, *128*, 6790. (f) Wang, D.-H.; Hao, X.-S.; Wu, D.-F.; Yu, J.-Q. *Org. Lett.* **2006**, *8*, 3387. (g) Ye, Z.; Wang, W.; Luo, F.; Zhang, S.; Cheng, J. *Org. Lett.* **2009**, *11*, 3974. (h) Liu, C.; Tang, S.; Zheng, L.; Liu, D.; Zhang, H.; Lei, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 5662. (i) Xie, P.; Xie, Y.; Qian, B.; Zhou, H.; Xia, C.; Huang, H. *J. Am. Chem. Soc.* **2012**, *134*, 9902. (j) Rout, S. K.; Guin, S.; Banerjee, A.; Khatun, N.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2013**, *15*, 4106. (k) Rout, S. K.; Guin, S.; Ali, W.; Gogoi, A.; Patel, B. K. *Org. Lett.* **2014**, *16*, 3086.

- (4) (a) Pappas, C. S.; Malovikova, A.; Hromadkova, Z.; Tarantilis, P. A.; Ebringerova, A.; Polissiou, M. G. *Carbohydr. Polym.* **2004**, *56*, 465. (b) Aliboni, A.; D'Andrea, A.; Massaniso, P. *J. Agric. Food Chem.* **2011**, *59*, 282.

- (5) (a) Khan, K. M.; Maharvi, G. M.; Hayat, S.; Zia-Ullah; Choudhary, M. I.; Atta-ur-Rahman, A. *Tetrahedron* **2003**, *59*, 5549. (b) Kesavan, L.; Tiruvalam, R.; Ab Rahim, M. H.; bin Saiman, M. I.; Enache, D. I.; Jenkins, R. L.; Dimitratos, N.; Lopez-Sanchez, J. A.; Taylor, S. H.; Knight, D. W.; Kiely, C. J.; Hutchings, G. J. *Science* **2011**, *331*, 195. (c) Liu, H.; Li, Y.; Jiang, H.; Vargas, C.; Luque, R. *Chem. Commun.* **2012**, *48*, 8431. (d) Huang, J.; Li, L.-T.; Li, H.-Y.; Husan, E.; Wang, P.; Wang, B. *Chem. Commun.* **2012**, *48*, 10204. (e) Feng, J.; Liang, S.; Chen, S.-Y.; Zhang, J.; Fu, S.-S.; Yu, X.-Q. *Adv. Synth. Catal.* **2012**, *354*, 1287. (f) Liu, L.; Yun, L.; Wang, Z.; Fu, X.; Yan, C.-H. *Tetrahedron Lett.* **2013**, *54*, 5383. (g) Majji, G.; Guin, S.; Gogoi, A.; Rout, S. K.; Patel, B. K. *Chem. Commun.* **2013**, *49*, 3031.

- (6) (a) Rout, S. K.; Guin, S.; Ghara, K. K.; Banerjee, A.; Patel, B. K. *Org. Lett.* **2012**, *14*, 3982. (b) Liu, H.; Shi, G.; Pan, S.; Jiang, Y.; Zhang, Y. *Org. Lett.* **2013**, *15*, 4098.

- (7) For selected reviews, see: (a) Giri, R.; Shi, B.-F.; Engle, K. M.; Mangel, N.; Yu, J.-Q. *Chem. Soc. Rev.* **2009**, *38*, 3242. (b) Wang, D.-H.; Engle, K. M.; Shi, B.-F.; Yu, J.-Q. *Science* **2010**, *327*, 315. (c) Colby, D. A.; Bergman, R. G.; Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624. (d) Lyons, T. W.; Sanford, M. S. *Chem. Rev.* **2010**, *110*, 1147. (e) McMurray, L.; O'Hara, F.; Gaunt, M. J. *Chem. Soc. Rev.* **2011**, *40*, 1885. (f) Gutekunst, W. R.; Baran, P. S. *Chem. Soc. Rev.* **2011**, *40*, 1976. (g) Baudoin, O. *Chem. Soc. Rev.* **2011**, *40*, 4902. (h) Engle, K. M.; Mei, T.-S.; Wasa, M.; Yu, J.-Q. *Acc. Chem. Res.* **2012**, *45*, 788. (i) Rouquet, G.; Chatani, N. *Angew. Chem., Int. Ed.* **2013**, *52*, 11726.

- (8) For selected examples, see: (a) Dick, A. R.; Hull, K. L.; Sanford, M. S. *J. Am. Chem. Soc.* **2004**, *126*, 2300. (b) Hull, K. L.; Anani, W. Q.; Sanford, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 7134. (c) Campeau, L.-C.; Schipper, D. J.; Fagnou, K. *J. Am. Chem. Soc.* **2008**, *130*, 3266. (d) Novák, P.; Correa, A.; Gallardo-Donaire, J.; Martin, R. *Angew. Chem., Int. Ed.* **2011**, *50*, 12236. (e) Iglesias, A.; Alvarez, R.; de Lera, Á. R.; Muñoz, K. *Angew. Chem., Int. Ed.* **2012**, *51*, 2225. (f) McMurtrey, K. B.; Racowski, J. M.; Sanford, M. S. *Org. Lett.* **2012**, *14*, 4094. (g) Liu, B.; Zhou, T.; Li, B.; Xu, S.; Song, H.; Wang, B. *Angew. Chem., Int. Ed.* **2014**, *53*, 4191.

- (9) (a) Xie, Y.; Yang, Y.; Huang, L.; Zhang, X.; Zhang, Y. *Org. Lett.* **2012**, *14*, 1238. (b) Ju, L.; Yao, J.; Wu, Z.; Liu, Z.; Zhang, Y. *J. Org. Chem.* **2013**, *78*, 10821.

- (10) (a) Zaitsev, V. G.; Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2005**, *127*, 13154. (b) Shabashov, D.; Daugulis, O. *J. Am. Chem. Soc.* **2010**, *132*, 3965. (c) Zhang, S.-Y.; He, G.; Nack, W. A.; Zhao, Y.; Li, Q.; Chen, G. *J. Am. Chem. Soc.* **2013**, *135*, 2124.

- (11) (a) Racowski, J. M.; Dick, A. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 10974. (b) Deprez, N. R.; Sanford, M. S. *J. Am. Chem. Soc.* **2009**, *131*, 11234.

- (12) (a) Powers, D. C.; Geibel, M. A. L.; Klein, J. E. M. N.; Ritter, T. *J. Am. Chem. Soc.* **2009**, *131*, 17050. (b) Powers, D. C.; Ritter, T. *Nat. Chem.* **2009**, *1*, 302. (c) Mazzotti, A. R.; Campbell, M. G.; Tang, P.; Murphy, J. M.; Ritter, T. *J. Am. Chem. Soc.* **2013**, *135*, 14012.

- (13) (a) Kornblum, N.; DeLaMare, H. E. *J. Am. Chem. Soc.* **1951**, *73*, 880. (b) Zhang, M.; Liu, N.; Tang, W. *J. Am. Chem. Soc.* **2013**, *135*, 12434. (c) Zhang, J.; Jiang, J.; Xu, D.; Luo, Q.; Wang, H.; Chen, J.; Li, H.; Wang, Y.; Wan, X. *Angew. Chem., Int. Ed.* **2015**, *54*, 1231.

- (14) (a) Shi, Z.; Zhang, C.; Tang, C.; Jiao, N. *Chem. Soc. Rev.* **2012**, *41*, 3381. (b) Gowrisankar, S.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 5139.